



Current and future aspects of bioethanol production and utilization in Turkey



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ABSTRACT

This study aims to present a comprehensive review on the production of bioethanol, both the first and second generation in Turkey and future aspects regarding R & D studies, standards, and statutory regulations. Due to the primary energy demand in Turkey, petroleum becomes prominent, which is almost wholly exported and causes the emissions of greenhouse gases such as CO₂, CO, CH₄ and NO_x. As an alternative fuel, and to match the convenient features of petroleum, bioethanol has been considered, and has become a large research area in order to improve production from plant residues known as second generation bioethanol (SGB). Instead of first generation bioethanol, producing and using SGB is highly recommended according to sustainability, development, and the domestic economy. Alternative fuels became more prominent in Turkey after Turkey signed the protocol to the United Nations Framework Convention on Climate Change (UNFCCC). Also, according to Turkey's Intended Nationally Determined Contributions (INDCs) report Turkey will carry on studies to increase the usage of wastes to produce alternative fuel at the appropriate sectors, promote alternative fuels and clean vehicles, and reduce fossil fuel consumption. When Turkey's biomass potential and dependence on foreign energy sources are taken into account, bioethanol production and utilization become prominent. Although, Turkey still produces bioethanol from corn, sugar beet, and barley, it falls short of total gasoline consumption. Lignocellulosic materials should be thought as alternative to first generation, and R & D studies should improve how to optimize second generation bioethanol production in the name of decreasing the total process cost.

1. Introduction

Petroleum and natural gas are the most important and primary energy sources for Turkey like rest of the world. Transportation and industry are mostly based on these fossil energy sources. However, as is well-known, the emissions from petroleum cause greenhouse gases and implications in regard to climate change. While it is known that energy is a critically important component in industry, and contributes to long-term economic growth, fossil energy sources emissions are also a threat for sustainability. For these reasons, most countries decided to reduce greenhouse gas emissions. On 11 December 1997, The Kyoto Protocol was adopted in Kyoto, Japan, and entered into force on 16 February 2005 by the Protocol to the United Nations Framework Convention on Climate Change (UNFCCC). Including Turkey, 192 countries signed (191 states and 1 regional economic integration organization) this protocol, and began to reduce greenhouse gases emissions based on the premise that global warming exists and man-made CO₂ emissions have caused it [1]. However, Turkey, which is listed in Annex I to the UNFCCC, has been recognized as having

exceptional circumstances, and was, placed in a different situation than the other parties included in Annex I. As Turkey was not a party to the UNFCCC at the time the Protocol was adopted, it was not included in the Annex B of the Protocol which defined quantified emissions limitation or reduction commitments for Annex I parties. Therefore, Turkey does not have a quantified emissions limitation or reduction commitment in the first commitment period between the years 2008–2012 under the Protocol [2]. In December 2015, UNFCCC organized a meeting and invited all countries that had signed the UNFCCC to the “2015 United Nations Climate Change Conference”, which was held in Paris, France as a term “Intended Nationally Determined Contributions (INDCs)”. In this event, Turkey also submitted their own INDCs just as the other 132 countries had done. The main topic of the meeting was preventing the increasing average global temperature to more than 2 °C, and to reap the many benefits that arise from a necessary global transformation for clean and sustainable development [3]. According to Turkey's INDCs, total greenhouse gas emissions will be reduced up to 21% by 2030. Turkey will implement or contribute to this effort between 2021 and 2030. It covers energy, industrial processes and

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products use, agriculture, land use land-use change and forestry, and the waste sectors. According to Turkey's plan, reported in the "Republic of Turkey, Intended Nationally Determined Contribution, related to bioethanol, Turkey will carry out studies to increase use of waste as an alternative fuel in the appropriate sectors, promote alternative fuels and clean vehicles, and reduce fuel consumption and emissions of road transport with the National Intelligent Transport Systems Strategy Document (2014–2023) and its Action Plan (2014–2016), reuse, recycle, and use of other processes to recover secondary raw materials in order to utilize them as an energy source, or to remove wastes, to recover energy from waste by using processes such as material recycling, bio-drying, bio-methanization, composting, advanced thermal processes or incineration, the utilization of industrial wastes as an alternative raw material, or alternative fuel in other industrial sectors through industrial symbiosis approach. Turkey announced a reduction in greenhouse gas emissions from 1175 to 929 million ton CO₂ equal in 2030 [4]. These obligations bring strict responsibilities in order to start new research and to improve the current methods to produce renewable and domestic energy. When Kyoto Protocol, Turkey's INDC report and the primary energy demand in Turkey are taken into account, utilization of renewable energy resources instead of fossil energy sources became prominent. Bioethanol is distinguished depending on its similar properties to gasoline. Also, the reasons for the increased interest in biofuels and bioethanol can be grouped as follows;

1.1. Increase in technological developments such as product cultivation and transformation methods

The raw material to be used in the production of biofuels can be supplied at a cheaper price and can be converted into higher yields. In other words, in the production of cheap and highly efficient bioenergies, the total cost can come to a position where it can compete with the fossil energies commonly used today. In addition, with the development of technology, it will be possible to obtain more than one product instead of a single product in the process.

1.2. Development of the agricultural sector

National regulations are being made for raw materials to be used for the production of biofuels, production costs and producers. Livestock farming, agricultural activities and forestry products differ according to the climate and geographical conditions of the countries. However, it is expected that employment and production in the agriculture sector will increase and the local economy will improve as well, in case the ideal raw material cultivation for each region is promoted and product procurement is applied.

1.3. Global climate change

Greenhouse gases arising from the use of fossil fuels are increasingly released into the atmosphere every day. Countries have established obligations and sanctions in the light of their work and foresight on sustainability. It is known that the use of biofuels can reduce carbon dioxide (CO₂), which has a large share, especially in greenhouse gases. In particular, the resulting CO₂ from the plants is treated as atmospheric CO₂ in the photosynthetic cycle of the plant. In this case, it is stated that plants will be able to photosynthesize using this CO₂, the amount of CO₂ in the atmosphere will remain constant and there will be no increase in the amount [5].

This study investigates the Turkey's bioethanol production and utilization situation, and future prospects about improving the current status of bioethanol.

2. Bioethanol properties and historical development

Bioethanol can be used in gasoline vehicles, as the pharmaceutical

sector is also preferred in cosmetic and industrial processes, and that's why there is an increase in the amount of production every year on a global scale [6]. The reason for the bioethanol to come to the fore is not that it is just an alternative to the gasoline. Global consciousness initiated against fossil fuels surrounding the environment and attempting to reduce greenhouse gas emissions to the lowest are also criteria that increase the importance of bioethanol [7].

When bioethanol compared with gasoline; it is seen that bioethanol has higher octane number, higher burning limit and speed, higher evaporation temperature. Because of these properties, bioethanol can be used as a fuel in engines, resulting in a higher compression ratio and the least damage to the motorcycle can be reduced. However, because of its bioethanol structure, it also has a lower energy density than gasoline. The energy density of bioethanol is 33% lower than that of gasoline. Furthermore, the high probability of corrosion, low combustion luminescence and high tendency to easily form an azeotropic mixture with water are among the disadvantages of bioethanol [8].

Bioethanol provides more efficient combustion in the vehicle engine with approximately 35% oxygen content. As a result of this more efficient combustion, NO_x, hydrocarbons and particle emission values are observed to decrease. The resulting combustion CO₂ is not an extra released gas to the environment, as the bioethanol is produced from biomass sources. Emission CO₂ is captured by plants and used in photosynthesis reactions. Thus, there is no increase in the amount of net CO₂ in the atmosphere [9].

In addition to the use of bioethanol as an alternative fuel to petrol, studies are also being made on the use of diesel-biodiesel-bioethanol mixtures in diesel engines. With this mixture called e-diesel, the effects of adding ethanol on the diesel fuel cetane and octane number are investigated and applied on oxygen combustion efficiency and performance values [10–13].

The term of bioethanol means, unlike synthetic production methods, ethanol is obtained by biomass by biological methods. The widespread use of bioethanol as a fuel has increased in the 20th century. But the first use of ethanol in engines was in 1826 and 1876 by Nicolaus Otto, the inventor of the modern four-cylinder internal combustion engine. In addition, the popularity of ethanol used in lamps for lighting purposes in the 1850s was reduced due to the high usage tax at the time of civil war. In 1908, just after the tax cuts, ethanol was used as fuel in the model named "T" manufactured by Henry Ford. In the 1920s and 1930s, it began to be used as an octane enhancer in gasoline and to be used on vehicles in certain proportions. Especially during the Second World War, its importance and use increased due to the necessity that is near [14].

During World War II, the Japanese used a mixture of bioethanol and gasoline on their warplanes in order to meet their fuel needs. Between 1937 and 1944, the amount of bioethanol production is reported to be about 170 million liters per year. At that time, the use of ethanol as a fuel has become so widespread that the share of bioethanol production in liquid fuels has increased to 26.7%. However, the decline in oil prices following World War II has limited to the production of bioethanol [15].

Due to the serious oil crisis between 1973 and 1979 and therefore the increase in the unit price of gasoline, the use of bioethanol as fuel has been on the agenda again. Today, Brazil and America, which are still pioneers, have gone to serial ethanol production in 1975 and 1978, respectively, by developing the ethanol production industry with the program named "Proalcool" [16]. Despite the intensive effort and production of America and Brazil, the failure of other countries to come to alternative biofuels, especially bioethanol, has led to the inability of bioethanol to develop sufficiently on a global scale. Along with the increase in agricultural product quality and prices in the 1980s, falling oil prices constituted a major obstacle to ethanol production [17].

Today's ethanol industry has emerged in the 1990s, when oil prices began to rise and gasoline and other gasoline-type harms to the environment. Corn has become a basic raw material for an ethanol

production process. The easy growing of corn and the high efficiency of ethanol conversion make it the most important raw material. In the early 1980s in the production of ethanol, which is common in America, federal and regional legislators increased the value of ethanol by keeping the ethanol price lower than that of gasoline, and giving incentives. This event also helped farmers to start producing ethanol in order to add value to corn breeding with the so-called "Minnesota Model" deal [18]. The Minnesota Model is an agreement between local public institutions and the private sector, which aims to increase the value of agricultural products and to provide economic and social benefits to people by creating jobs in different fields. The use of ethanol as an oxygenator to control CO emissions has started in the 1990s with the Kyoto Protocol [19].

3. World and Turkey's current status

During World War II, ethanol production facilities have been constructed in some countries, such as Germany, Russia, China, Korea, Switzerland and the United States, using cellulosic resources, as war conditions have begun to change economies and priorities. It is aimed to sell the ethanol produced in these facilities as fuel to other countries and to meet the need of fuel by this way. With the end of the war, the production of synthetic ethanol has caused the closure of cellulosic ethanol production facilities [20]. In April 2004, a sample production facility using the first lignocellulosic raw material was operated in Canada [21]. In 2006, Brazil commissioned more than 300 bioethanol production facilities to produce 15 billion liters of pure bioethanol per year, which could be used in 3 million cars. In America, 10 billion liters of bioethanol was produced in more than 80 establishments over the same years. However, in 2008, the US rose sharply to the top in global ethanol production. Europe has a 5% share in total ethanol production, while Germany and France have the highest share [22].

In addition to the increase in new research, investment and production facilities worldwide for second generation bioethanol production, currently, mostly agricultural products and sugarbeet are used in Europe [23]. In the world leader USA, ethanol is produced with starch hydrolyzed from corn, and in the second order in Brazil, sugar is extracted and ethanol is produced from sugar cane derivatives [24].

The world's consumption of fossil fuels by transportation sector accounts for 60%, which consequently contributes to the massive pollution generation to the environment [25]. Due to this environmental problem, many countries take into account the renewables in total energy consumption; such as photovoltaics, wind turbines, and biomass energy. Alongside of the other renewable energy resources, which are mostly used to generate electricity, bioethanol become prominent due to being renewable and sustainable transportation liquid fuel that is expected to have a promising future in tackling today's global energy crisis and the worsening environment quality. According to Alternative Fuels Data Center reports, USA produced 58% of world's total bioethanol in 2015, while Brazil produced 28%. Europe and rest of the world only share 14% of bioethanol production [26]. According to the 2015 global bioethanol production report, production increased by 4% to reach 98.3 billion liters compared to 2014. The reason for this increase is that countries with world leaders in ethanol production can perform more efficient agricultural activities for raw material cultivation [27].

In 2006, Brazil activated more than 300 bioethanol facilities and produced 15-billion-liter pure ethanol which can be used in 3 million cars, while United States only produced 10-billion-liter bioethanol at over 80 facilities. However, in 2008 United States increased bioethanol production and usage rate on transportation and placed in number 1 in the whole world [28].

Turkey is a developing upper-middle income country according to the World Bank classification. Industry is growing fast and hence more energy is needed. Also, as a consequence of the wealth level and

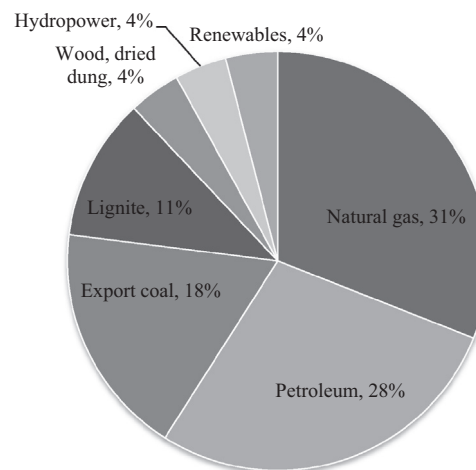


Fig. 1. Turkey's primary energy demand for 2013 (ETKB).

purchasing power improvement; the number of transportation vehicles is also increasing. That requires more fuel and causes more emissions. Today, the main energy sources Turkey uses are fossil fuels: petroleum, coal, and natural gas, and these classical energy sources are consumed much faster than their natural production (Fig. 1) [29]. Turkey is the highest increasing energy usage country in OECD, and it is mostly foreign-dependent on energy sources; especially in terms of petroleum and natural gas. Electricity is mostly generated by thermal power plants by using coal, lignite, natural gas, and fuel oil. The production of electricity from renewables is small. As for nuclear power, it is new and very limited [30].

Turkey exported 71.5% of the total energy that was used in 2012, and that value increased up to 73.5% in 2013, while the domestic energy sources' share was 26.5% in total primary energy consumption. Besides, from 1990 until 2013; the primary energy demand increased to 127.39% and exportation increased by 211.62%, while the national energy production increase was limited to 27.78%. Turkey's primary energy consumption shares in 2013 was; 26% housing, 26% conversion sector (generation), 25% industry, and 19% transportation, respectively. In 2014; however, 49,000 barrel/day of crude petroleum production was performed, and 718,000 barrel/day crude petroleum was consumed [31].

According to the projections of the Ministry of Energy and Natural Resources report, Turkey's total electricity (power) demand has been increasing rapidly and it reached 264 TWh in 2015. Natural gas accounted for 37.8% of total electricity generation in 2015. The structure of other energy sources used for electricity generation in 2015 was coal (28.4%), hydro (25.8%), wind (4.4%) geothermal (1.3%), fuel oil, diesel and naphtha (1.6%), and biogas (0.6%). By the end of 2015, the installed power capacity of Turkey has almost reached 74,000 MW of which 35.4% consisted of hydro power, followed by natural gas (28.7%), coal (21.3%), wind (6.2%), multi fueled (5.9%), geothermal (0.8%) and other sources (1.7%). Turkey imports nearly 99% of the natural gas it consumes, while imports around 89% of its oil supplies. In 2015, Turkey imported 25 million tons of crude oil in 2015 mainly from Iraq (45.6%), Iran (22.4%), Russia (12.4%) Saudi Arabia (9.6%), Colombia (3.5%), Kazakhstan (2.6%) and Nigeria (2.1%) [32].

Energy prices are considered as the issue with the most critical uncertainty in Turkey. This issue is related to the country's high rate of taxation for energy consumption, with 65% taxes on gasoline prices [33]. According to World Energy Council 2015 Energy Trilemma Index report [34] Turkey has maintained a stable position in the Index throughout the years (Table 1). The country balanced the three competing sides of the energy trilemma well, despite below average rankings in all three dimensions. With regard to energy security, the country's performance deteriorated slightly as oil and oil product

Table 1
Index rankings and balance score for Turkey [8].

| | 2013 | 2014 | 2015 | Score |
|---------------------------------------|------|------|------|-------|
| Energy performance | 74 | 71 | 82 | |
| Energy security | 64 | 63 | 71 | C |
| Energy equity | 82 | 76 | 73 | C |
| Environmental sustainability | 70 | 69 | 79 | C |
| Contextual performance | 68 | 69 | 62 | |
| Political strength | 65 | 68 | 70 | |
| Societal strength | 51 | 52 | 50 | |
| Economic strength | 91 | 95 | 71 | |
| Overall rank and balance score | 75 | 73 | 76 | CCC |

stocks decreases. The performance on the energy equity dimension did not display great changes as gasoline and electricity prices were stable. Turkey continued to struggle with mitigating its impact on the environment although some progress was reflected in slightly lower energy and emissions intensity, but progress in peer countries was faster. Contextually, Turkey's performance remained largely unchanged on the political and societal strength dimensions, but with a notable improvement in economic strength driven by a greater access to credit for the private sector.

According to climate and geographical pattern in Turkey; solar, wind, geothermal and biomass energy resources potentials differ from each seven regions, but it can say avowably that renewable energy sources in Turkey are the second largest source after coal in terms of energy production, and a significant portion of renewable energy production is met by biomass [35]. Almost all of the biomass energy is consumed mostly for cooking and heating purposes. Wood is the main heating fuel for 6.5 million residences in Turkey. The paper industry also uses wood wastes to provide 60% of the required energy for their production of plants [36].

Biomass is an important renewable energy in Turkey and its theoretical potential is about $5.66\text{--}6.29\text{Ejy}^{-1}$ [37]. When technical and economic aspects are taken into account, then the potential is about 1.05Ejy^{-1} . The potential of biomass raw material in Turkey is presented in Table 2 [38].

Bioethanol has an important place in all biofuels due to its similarity with gasoline, and has been considered as a potential alternative to the ever-reducing fossil fuels. The potential production of bioethanol in Turkey is about 800,000 l/day according to the existing bioethanol production plants [39]. There are 3 active bioethanol production facilities, and they use sugar beet, wheat, and corn (Fig. 2). Also, in view of Turkey's agricultural resources and their worth as food material, lignocellulosics shall be used as a biomass to produce SGB.

There are 12 plants producing bioethanol in Turkey, 8 of them have the capacity to produce biofuel, but only 3 of them are still producing bioethanol as fuel; the others use ethanol for beverages (Table 3) [40].

The Çumra Sugar Factory, a subsidiary company of Konya Sugar Factory, produces 84,000,000 l of fuel bioethanol in a year, and uses sugar beet, and black strap molasses. This factory produces 56% of installed bioethanol production capacity and delivers to petroleum distributors [41]. Sucrose-containing and starchy feedstocks and

Table 2
Biomass sources and their potentials [12].

| Resource | Raw material potential (million tons) |
|--|--|
| Municipal solid wastes | 25 |
| Wood | 3.52 |
| Forestry/wood processing | 3.56 |
| Agricultural residues-straw+stalk | 13.2 |
| Agricultural residues-seed, shells, wood chips | 4 |
| Fertilizer | 13.8 |

Nominal Ethanol Production Capacity (l/day)

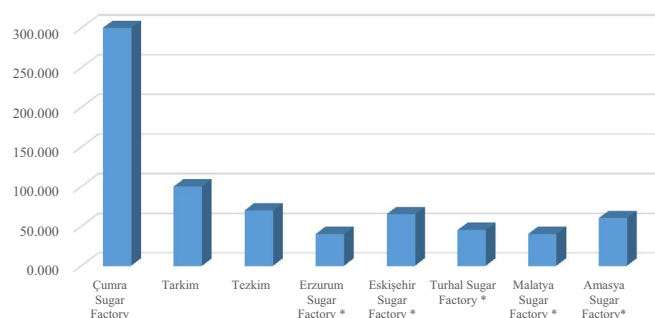


Fig. 2. Current production of bioethanol and total potential in Turkey, * only potential.

Table 3
Bioethanol Producer Factories/Corporations in Turkey [14].

| Factory/Corporation | City | Type of Bioethanol |
|--|----------------|--------------------|
| Allco Beverage Corp. ^a | İzmir | Ethyl alcohol |
| Amasya Sugar Factory | Amasya | Ethyl alcohol |
| Antalya Alcoholic Beverages ^a | Antalya | Ethyl alcohol |
| Infotex ^a | Afyonkarahisar | Ethyl alcohol |
| Konya Sugar Factory – Çumra Sugar Factory | Konya | Fuel bioethanol |
| Mey Alcoholic Beverages Factory ^a | Karaman | Ethyl alcohol |
| Tarkim | İstanbul | Fuel bioethanol |
| Tezkim | Adana | Fuel bioethanol |
| Erzurum Sugar Factory ^b | Erzurum | Ethyl alcohol |
| Eskişehir Sugar Factory ^b | Eskişehir | Ethyl alcohol |
| Malatya Sugar Factory ^b | Malatya | Ethyl alcohol |
| Turhal Sugar Factory ^b | Tokat | Ethyl alcohol |

^a Only produces for beverages-not fuel.

^b Belongs to Turkey Sugar Factories.

materials have a great bioethanol production potential. This factory also produces a by-product called distiller dried grains with solubles (DDGS). In the ethanol fermentation processes sugar, and the starch from the cereals is converted into bioethanol, and the left overs which contain high quantity protein, lipid, and sugar components are separated to use as feedstuff. DDGS has 30% dry matter and has mostly been used and/or added to cow feed [42]. Hence, produced DDGS is inadequate, Turkey exports almost all used DDGS, and the USA has the biggest part of the exportation share from Turkey [43].

Turkey's population is about 77.5 million, and 19% of this population is engaged in agriculture. Production amounts of cereals and other crops in 2014 that were used to produce bioethanol in Turkey are given in Table 4 below [44].

These crops are some of basic bioethanol raw material, but are also used for making food products such as bread, flour, sugar, and other goods. This situation brings those crops to a very important level in the food chain. Also, after the processing of them, the residues are used for animal feedstock. If all these conditions are taken into account, utilization of lignocellulosic's materials or invaluable crop residues could be used in bioethanol production instead of agricultural crops.

4. Bioethanol related policies in Turkey

Beginning from the 1990s, natural gas and petroleum had expan-

Table 4
Chosen crops produced in Turkey could be used for bioethanol production in 2014 (Tons) [18].

| Wheat | Barley | Maize | Sugar beets |
|------------|-----------|-----------|-------------|
| 19,000,000 | 6,300,000 | 5,950,000 | 16,572,790 |

sion in the use for power generation and residential-commercial heating sectoral. Thus, The Turkish government plans to reduce the country's dependency on petro-based road transportation fuels by blending biofuels with gasoline and diesel.

Gasoline used in Turkey is the most expensive petrol used in all OECD countries in terms of price. The reason of this is that the imported fuels are subject to high taxes in our country [45].

Bioethanol has rarely been used in Turkey with the Petrol Office (PO) being the only firm that used the ethanol until 2011 since it was legally allowed to embed up to 5%, which is the amount of the ethanol addition in gasoline, and only 2% ethanol could be added because of the high level of taxes. Also, gasoline prices are really high in Turkey, almost the highest price in the world, so using bioethanol should be considered instead of gasoline [46].

The Republic of Turkey Energy Market Regulatory and Authority (EPDK) has adopted a course of action regarding using agricultural products as a raw material for biofuel production to promote the local biofuel production and to decrease current deficit. According to this 2013 decision, it is obliged to embed biofuels ever-increasingly from local agricultural products (bioethanol and biodiesel) over the years. Dating from January 1st, 2013, the local content rate in gasoline is going to be 2%, and dating from January 1st, the 2014 local content rate in gasoline is going to be at least 3% [47].

5. Bioethanol production

Bioethanol production is a biological process performed by micro-organism in required medium and conditions. Therefore, selection of microorganisms is of great importance in bioethanol production. Microorganisms should be chosen by the composition of the raw material, and the optimization conditions required for the selected technique. The yeast and bacteria commonly used in industrial ethanol production have advantages and disadvantages compared to each other in this area. The most interesting of the studies carried out today is the studies on biocatalysts that can efficiently ferment mixed sugar fractions. Some of these are *Pichia stipitis*, which provides xylose fermentation in ethanol production, *Escherichia coli*, *Kluyveromyces* species, which allow the use of pentosone with *Zymomonas mobilis*, and other yeast species of *Saccharomyces cerevisiae* and *Saccharomyces* species. In addition to these, thermophilic bacterium *Clostridium thermocellum*, which can metabolize the cellulose structure, and white rot fungi, which degrade lignin, are also in the research [48–51].

5.1. First generation (Traditional) bioethanol

First generation bioethanol means converting sugar-based fermentation into ethanol by yeasts or other microorganisms such as bacteria. Mostly corn, wheat, barley, sugar cane and sugar beet are used. The USA is the global leader in producing bioethanol by using corn, and Brazil, China, Canada, and France follow the USA [52]. The fermentation of sugars is referred to as the first generation bioethanol process, where yeast is cultured under optimum conditions to convert sugars into ethanol at around 30 °C. The production of bioethanol from starch/sugar-containing materials takes place in four steps; pretreatment (hydrolysis/liquification-saccharification), fermentation, distillation, and dehydration. Sugar/starch containing materials are easy to obtain carbohydrates with lignocellulosic. Pretreatment and the dehydration steps are the key steps that affect bioethanol production efficiency and the total cost of the process. Physical, chemical, and enzymatically pretreatment methods can be used either separately or combined. The particle surface increasing (physical), concentrated/diluted alkali or acid pretreatment (chemical) and cellulosic/microbiological (enzymatically) treatments are the most chosen methods. The main aim is to put the carbohydrate source into the fermentation medium. The pretreatments take extra time, labor, and energy; hence,

it increases the total cost of the bioethanol production process. To minimize the total cost, the optimum conditions, the optimum amounts of chemicals, methods, and the optimum raw materials are used. The sugar/starch containing the raw materials' structure can be broken down easily not like the lignocellulosic materials. The main difference shows up in the first step; pretreatment; between the first and second generation bioethanol production according to the applied pretreatment and intensive methods [53].

5.2. Second generation bioethanol

Lignocellulosic biomass became one of the attractive alternative materials for bioethanol production. Lignocellulosic materials are the most abundant renewable resources on earth. The use of lignocellulosic materials would minimize the potential conflict between the land use for food and animal feed production, and energy feedstock production. Also, lignocellulosic materials are cheaper than traditional bioethanol raw materials, and can be grown with a lower input of fertilizers, pesticides, and energy [54]. Lignocellulosic raw materials such as residues of agriculture and forestry products, energy plants and aquatic plants can be supplied at a cheaper price than the raw materials used in the first generation in order to use the fuel for bioethanol production in the region where the lignocellulosic raw materials differ depending on the climate conditions. Global lignocellulosic biomass production is approximately 200×10^9 tonnes per year, while the potential residual amount from these products is It is estimated to be $8\text{--}20 \times 10^9$ t [55]. The use of lignocellulosic raw materials in ethanol production over the last 15–20 years has been the subject of considerable research and application studies [56,57]. Some of specific lignocellulosic materials, which can be used for bioethanol production process, are switch grass [58], corn cob [59], rice husk [60], wheat stem [61], and other agricultural residues.

In a SGB production process, the pretreatment is the major step according to obtain as much as carbohydrate from the lignocellulosic material. With an effective pretreatment method, the chemical bonds between lignin, cellulose and hemicellulose structures can be broken down to release polysaccharides, while preventing inhibitor formation [62–64].

Although it has been considered that SGB is a better way to obtain bioethanol than the first generation, the process still has some limitations because of technical and economic challenges. The first challenge is the formation of some of the inhibitors depending on the lignocellulosic structure while the pretreatment step causes problems during the fermentation [65]. The second challenge is that it is obligatory to use enzymes to break down cellulose structure to obtain carbohydrate. Enzymes are still expensive and that causes an increase in the total cost of the SGB production process [66]. Also, some microorganisms; such as *Clostridium thermocellum*, white fungi etc., are being used instead of enzymes. Those microorganisms produce extracellular or intracellular cellulolytic secretion to hydrolyze cellulose and use that carbohydrate source to produce bioethanol. However, those organisms need special conditions for inoculation, activation, and fermentation. The third challenge interests both the first and second generation; dehydration step, and its process cost. To use bioethanol as a biofuel, it needs to contain at least 99% ethanol purity, and this step requires more energy and some expensive chemicals and/or equipment. If these challenges are considered, developing countries, especially those that have just started to produce traditional first generation bioethanol such as Turkey, need more R & D studies and improvement of the current process.

What is important in the second generation bioethanol production is to reduce production costs in all possible steps. In conventional ethanol production methods, free yeast cells and batch reactors are used. The bioreactor is filled with the prepared fresh medium (carbohydrate source), and after the fermentation, the whole volume is again drained. Performing the filling and unloading each time causes a

decrease in the volumetric yield of ethanol production as well as time and energy losses. Instead, the use of continuous systems and immobilized systems appears to be more advantageous. Continuous fermentation systems have advantages such as high conversion efficiency, constant quality of product and reduction of product losses. In continuous systems where immobilized columns are used; have advantages such as toxic preservation of cells, inhibition of high cell density, increased recovery of cells, and prevention of contamination from other microorganisms [67]. In the other hand, there are 4 alternative processes to produce bioethanol; simultaneous saccharification and fermentation (SSF), separate hydrolysis and fermentation (SHF), simultaneous saccharification and co-fermentation (SSCF), and Consolidated bioprocessing (CBP). All these process have some advantages and disadvantages, and the process is chosen by taking into consideration the raw material, microorganism, and final product(s).

One of the most costly inputs in the production of lignocellulosic ethanol is the cellulase enzyme used for the hydrolysis of lignocelluloses. About 100 g of enzyme should be used in the 3.8 l (1 gallon) of cellulosic ethanol production. 100 g highly active pure enzymes are worth an average of 200–300 US Dollars [68]. In order to compensate for the high cost of cellulase, it is necessary to increase the volumetric production and reduce the total process cost. In this case, combined bioprocess (CBP) antagonism emerges as a method to be improved and improved.

It should not be forgotten that Turkey's biomass energy potential is about 32 Mtoe. The amount of usable biomass potential in Turkey is approximately 17 Mtoe [69]. The SGB production process and optimization have been researched by several researchers in Turkey. Demirbas [70] proposed that lignocellulosic materials provide a potential source of added value chemicals, such as reducing sugars, furfural, ethanol and other products, by using biochemical or chemical and thermochemical. Balat et al. [71] suggested that using lignocelluloses instead of cereals to reduce the total cost of bioethanol production. Balat [72] suggested producing bioethanol from cellulose feedstocks such as corn stalks, rice straw, sugar cane bagasse, pulpwood, switch grass, and municipal solid waste; hence, up to 80% of the production cost is the cost for feedstock. Arslan and Eken-Saraçoğlu [73] in their study analyzed the pretreatment effects on both lignocellulosic bioethanol production and its efficiency. İsci [74] proposed that the total lignocellulosic biomass could produce up to 6.10 Gl of bioethanol per year in Turkey. The potential bioethanol production could replace 4.39 Gl of gasoline per year when bioethanol is used in E85 fuel for a midsize passenger vehicle. Imamoglu and Sukan [75] studied and published a paper about optimization SGB production by ice hulls hydrolyzate and recombinant *E. coli* KO11, and reported the findings of the research, which could contribute to the industrial scale productions; especially from lignocellulosic raw materials. Theoretical and lab scale studies are still being carried out by universities, some research companies, and other governmental facilities in Turkey. An industrial scale lignocellulosic bioethanol production process and system is up and coming, and is needed to be researched exclusively for the situation in Turkey.

6. Conclusions and future aspects

Turkey is a developing country and its industry is continually increasing; hence, the energy demand is also gradually increase. Although Turkey has a high usage and potential of renewables, still using fossil fuels substantially. This causes environmental pollution and threatens sustainability. Turkey has signed the Kyoto Protocol with some eligibility, but still needs to reduce greenhouse gas emissions and propose to use renewables in industry, agriculture, and transportation. Every year, Turkey imports energy from abroad and the costs are high. Turkey imports more than 90% of its petroleum and already consumed 72.8% of its proved reserves, and forecasting based on production. This imported energy is mostly used for transportation; generating electric-

city and heating. Meanwhile, the number of vehicles on the road is continually increasing, and correspondingly transportation fuel demands increases. There is a significant alternative fuel to gasoline; bioethanol. It is clean, domestic, and renewable fuel, has similar properties to gasoline, and supports national and global sustainability. Agricultural products are used in the ongoing first generation bioethanol production in Turkey, but it should be changed into second generation to avoid the use of food raw materials which are important to the public. Lignocellulosic biomass enables this opportunity, and has become prominent due to its inexpensiveness. Otherwise, pretreatment and obtaining a carbohydrate source is harder than the sugar/starch containing biomass. The fine tuning of pretreatment technologies for different biomass types and the development of an economically viable process are still needed. To optimize all of the parameters in order to utilization of ethanol production from lignocelluloses, still theoretical and lab scale studies are still being carried out by universities, some research companies, and other governmental organizations in Turkey. When Turkey's biomass potential and dependence on foreign energy sources are taken into account, bioethanol production and utilization become prominent. Although, Turkey still produces bioethanol from corn, sugar beet, and barley, it falls short of total gasoline consumption. Lignocellulosic materials should be thought as alternative to first generation, and R & D studies should improve how to optimize second generation bioethanol production in the name of decreasing the total process cost.

The widespread use of bioethanol in the long term is of great importance in terms of reducing the environmental pollutants, especially caused by fossil fuels, and ensuring sustainability. With the increased use of bioethanol in transportation, the emissions, such as particulate matter and NO_x, in exhaust gases can be limited, and a reduction of 21% of greenhouse gas emissions by 2030, which Turkey presents in the INDC report, could contribute to its predictions. Along with the increased use of bioethanol, it is expected that the required production capacity will increase and new investments will be made after exist three ethanol factories established in our country. Thus, it would be possible to create a new industry and contribute to the economy of the country by generating employment and domestic fuel production.

Considering all these situations, Turkey should improve first generation bioethanol, increase its number of facilities, implement more policies, but the most important recommendation could be to start the industrial scale lignocellulosic bioethanol production process studies; which are not in competition with food and animal feed.

The fact that ethanol can be used as an alternative to gasoline, and even in diesel engines, is a feature of biofuels. For this reason, the widespread use of bioethanol will lead to a decline in fossil fuels and a positive impact on sustainability. In addition, when considering the social and economic structure of our country based on the agricultural and socioeconomic structure, especially the vegetation residues which are not used in the human food chain and which are not used as animal feed, collected at least twice a year and burned on the agricultural land, especially when the climatic conditions and soil structure of Turkey are examined, instead of this traditional burning method of energy conversion and elimination of waste, bioethanol production will provide a great socio-economic gain. Considering the information for Turkey, wheat straws which are concentrated in rural areas, water hyacinth, which have an important place in natural water treatment, and other lignocellulosic (agricultural and other) residues are used as raw materials in the second generation bioethanol production. When these bioethanol production processes are promoted as SHF and *Saccharomyces cerevisiae* is used as the microorganism, it is predicted that the process will proceed in the appropriate conditions and with good efficiency. It has also been observed that, in these processes, the cellulase enzyme may be suitable for use alone without chemical pretreatment. It is believed that for large-scale systems where continuous production is to be achieved, the use of yeast strains such as *S.*

Cerevisiae and *P. stipitis*, which are used in the experiments, will be an advantage in cell recycling by replacing bacteria that operate in more difficult ambient conditions such as *C. thermocellum*.

One of the most important parameters in the production of lignocellulosic bioethanol is that the microorganism used has the ability to ferment sugar as different as possible for the efficient transformation of the biomass. Although the biochemical ethanol production process is not deeply well-known, the physiological pressures that limit glycolysis and ethanol production are still under investigation. The identification of these pressures will be an important step in the development of process conditions and the use of microorganisms. These developments may be able to increase the ethanol production capacities of existing fermentation units, thereby reducing the cost of future processes.

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